REMOVAL OF **RESIDUAL CHAR FINES FROM PYROLYSIS VAPORS BY HOT GAS FILTRATION**

J. SCAHILL, J. P. DIEBOLD, and C. FEIK
National Renewable Energy Laboratory
Center for Renewable Chemical Technologies and Materials
Golden, Colorado, USA

Abstract
An NREL-designed vortex reactor fast pyrolysis process development unit (PDU) has been used to investigate hot gas filtration of biomass pyrolysis vapors. Most of the experimental work employed a conventional baghouse type of filter that used NEXTEL™ ceramic cloth filter bags as the filter medium.

   A series of experimental runs demonstrated that hot gas filtered biocrude oils having less than 10 ppm of total alkali could be reproducibly made. Removal of the char cake from the filter elements proved to be a difficult problem. The char appears to become progressively more sintered to itself and the filter as a function of the cumulative biomass processed. Controlled oxidation does remove this dense char from the filters, but leaves residual ash on the filter cloth fibers. This ash may in turn cause subsequent biomass pyrolysis vapors that pass through the filter to produce additional char (coke) in the interstices of the filter cloth. Data are presented that suggest this char formation may contribute to a more rapid rise in the rate of filter blinding as measured by the increase in recovered filter pressure drop.

1 Introduction

The use of biomass pyrolysis oils in relatively sophisticated applications, such as power generation via gas turbines or diesel engine generators, has attracted increasing interest in recent years. These applications hold the promise of providing cost-effective markets for this form of renewable energy from biomass. Fuels used in these systems are required to meet specifications related to their physical, chemical, and combustion properties that affect the reliable long term operation of the application equipment. The more important properties are viscosity, ash, alkali metal content, heating value and Cetane number. Pyrolysis oils must be produced in such a manner that they will consistently meet the standard specifications required by the end-use application.
   It has been long recognized that the physical properties of biomass pyrolysis oils

change over extended periods of time. Recent studies have reported the rate of this change [1], which is characterized primarily by increases in average molecular weight and water content. When molecular weight increases, viscosity also increases. Other recent work has linked the presence of char fines in the oil to this viscosity increase [2]. Char has also been identified as the source of alkali metal, a contaminate that limits the use of pyrolysis oil in turbine applications [3]. Thus, the presence of char fines degrades the quality of pyrolysis oils and weakens their ability to penetrate the higher quality fuel markets. To meet the specification requirements of the high value end-user applications, high quality pyrolysis oils having uniform, reproducible properties must be free of char fines.

Char fines originate in the fast pyrolysis processes that produce high yields of these oils from solid biomass feedstocks. During processing, char and pyrolysis gases are produced simultaneously with oil vapors and are usually co-mingled with the vapors in the resulting process stream. Most reactor designs employed to pyrolyze biomass subject the char to some degree of attrition, either from the heat transfer medium (fluidized beds and some entrained flow designs) or during particle acceleration (vortex type). The exception to this is the staged-hearth, vacuum pyrolysis reactor developed at the University of Laval in Quebec, Canada [4].

The low density char from these processes, typically a powder as a result of this attrition, usually is entrained in the gas and vapor stream exiting the reactor. Cyclone separators have traditionally been used to remove solid char particles from pyrolysis vapor/ gas streams because of their low cost and reliable design. However, a small but significant portion of the char from pyrolysis processes falls below 5` m particle size and consequently is not captured by cyclones. Filtration and electrostatic precipitators (ESP) are both effective at removing this size particle from the gas stream. ESPs are more expensive from both a capital and operating standpoint.

NREL has been developing the use of high temperature filtration for separating char fines from a pyrolysis gas/vapor stream for the past three years [5,5a]. Advantages to filtering the gas/vapor stream prior to condensation are viewed as follows:

> 1) The char and oil are discretely separated to enable each to be marketed individually.

> 2) Separation prior to condensation of the vapors eliminates the detrimental influence of char on long term oil stability.

> 3) This process eliminates the monetary and environmental costs of disposing of the liquid /solid sludge produced by filtering char from the oil.

The major technical disadvantage of hot gas filtration is a small yield penalty resulting from vapor-cracking reactions in the baghouse filter at the higher temperatures necessary to prevent condensation of the vapors. It appears that a compromise will need to be made between a superior quality oil and slightly lower yields.

Hot gas filtration is a relatively new technology, and most of the advances in systems

and materials have taken place since the early to mid 1980s [6]. Much of this work, which was focused on combustion and gasification processes, attempted to meet low particulate emission standards or specifications for the resulting gases. This early work, developed materials and designs that can withstand processing temperatures ranging up to 1000` C. Reliable long-lived filters and efficient particulate capture were the principal objectives of this development effort. Systems employing hot gas filtration and the operating principles involved have been presented in other publications and will not be redescribed here [7].

High temperature filtration in pyrolysis applications has different design constraints than those needed for combustion and gasification. The time/ temperature relationship of the vapors as they pass through the filter device is very important for pyrolysis. The optimum operating temperature is the lowest possible that will avoid condensing vapors on the filter cake or filter media. The dew point of this condensation is also a function of the amount of inert carrier gases present with the vapors. Residence time of the gas/vapor stream at elevated temperatures is generally not a concern for combustion or gasification processes, but it is a significant issue when the filtration is done on pyrolysis vapor streams. In conventional baghouse filter designs the volume adjacent to the filter elements is fixed at a minimum value based on the net gas throughput of the unit. If volume is too low, high gas velocities quickly re-entrain particles that have been dislodged from the filters following backpulsing. So, for any given system, the residence time is fixed, based on the design gas throughput. This gas throughput also establishes the face velocity or air to cloth ratio and the size (volume) of the vessel holding the filters [7]. For the gas/vapor velocities used in our process at NREL [5,5a], the residence time in the baghouse was approximately 5-6 seconds. In two separate runs using the same poplar feedstock, organic liquid yields increased from 36 wt% to 49 wt% (dry biomass basis) as the baghouse temperature was reduced from 410-450` C to 370-390` C. This may be the low end of the temperature range that can be safely used without condensing vapors on the filter, except for the case of relatively high carrier gas flow rates. However, it may be possible to reduce the residence time of the vapors by considering filter designs other than conventional baghouses.

2 Conventional Baghouse Filter

The filter used was a conventional baghouse filter designed with the minimum recommended volume and which employed flexible high temperature ceramic fiber cloth bags made by 3M as the filter medium. This cloth material (NEXTEL™), has a maximum operating temperature of 760` C (in the presence of alkali oxides). The oxides will melt above this temperature and form a glass that fuses to the fibers and cause them to become brittle [8]. The filter cloth has a nominal pore size of about 2` m, but in practice, it relies on the establishment of a cake of particles on the filter surface to actually do the separation of subsequent particles, especially the very small ones. The baghouse is fitted with four filter elements, each having a nozzle and venturi throat to provide a short pulse of gas inside the filter that imparts a rapid expansion front down the cloth bag to dislodge the cake when the pressure drop becomes excessive. This is

the same baghouse filter that was used at NREL [5,5a], but the gaseous residence time is about half that previously reported.

3 Experimental Process Conditions

The following is a description of the relevant operating conditions used for the experimental activities conducted with the two types of filters described above.

3.1 Vortex Reactor
The pyrolysis operating conditions used in all experimental runs were essentially the same:

`        Nitrogen carrier gas @ 650` C and 41 kg/hr flow rate (fixed for all runs)
`        Vortex reactor wall temperature @ 625` C
`        Vortex reactor exit gas/vapor temperature was initially at 520` C prior to feeding but equilibrated to 455` C at steady state feed conditions
`   Biomass solids feed rate varied from 17 kg/hr to 24 kg/hr depending on the specific run
`   Nitrogen carrier gas to oil vapor ratio: 3.6 to 2.6

3.2 Baghouse
The baghouse operating temperatures ranged from 385` C to 405` C at the entrance, which was controlled by the addition of liquid and/or gaseous nitrogen. This method of temperature control was quite good with deviations of only 3` - 4` C during a run. However, zone temperatures (bottom, middle, top) inside the baghouse typically varied by about 10` - 15` C; the top zone was consistently hotter.

3.3 Condensation Train
The condensation train was operated to reduce the gas/vapor stream to the lowest temperature possible. The initial stage of this temperature reduction occurs in the venturi scrubber where the gas/vapors enter at 360` -375` C and are quenched to 85` - 90` C when passed through the throat area concurrently with recycled biocrude condensates. When starting up without the benefit of the recirculated condensates this quenching occurs by a combination of recirculating cooled pyrolysis gases and heat transfer to water-cooled walls. This typically resulted in an exit temperature of about 200` C.  It usually required between 10-12 kg of feed to be processed before enough condensates were collected to begin the recirculation.  Following the venturi scrubber the process stream passes through two conventional shell and tube heat exchangers where the temperature is reduced to between -5` and +5` C before entering the coalescing filters.  This stream can rise to as much as 8` C at the exit of the filters. The gas/vapor stream usually starts out at the low end of this range and rises as the run progresses.

3.4 Feedstock

A hybrid poplar (*P. trichocarpa x P. deltoides*) was used for all these experiments [5,5a]. This biomass was obtained from the James River Paper Company and grown on the tree plantation that supplies feed to their pulp mill. The trees were harvested seven years into their growth cycle and debarked to a level of 1.0% bark remaining in the final dry chips. This feed is probably typical of that which would be obtained from a dedicated woody biomass energy farm. The chips were knife milled through a 3.2 mm screen and bone dried at 105` C before feeding to the process. Feedstock Analysis is shown in Table 1.
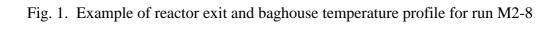
4 Process Operation Experience

Research collaboration and subcontract activities made it necessary to produce significant quantities of hot gas filtered biocrude oil. On a previous run with the baghouse filter (Run 175) we had demonstrated the ability to produce oils in reasonable yields with very low char levels. During this run two cyclones were used up-stream of the baghouse to remove the bulk of the char prior to the filter. This configuration pre-separated the coarser particles and sent only the very fine char to the filter which formed a denser cake that appeared to have sintered and was not removable by backpulsing. This phenomenon has also been observed in other hot gas filtering applications [9] where the cake is formed from a narrow particle size distribution of solids.

 With the baghouse in place, five runs (numbered 6 through 10) were conducted with the objective of producing quantities of biocrude having low char and alkali metal content. The current system was configured without the cyclones upstream of the baghouse so that a broad distribution of char particles would be sent to the baghouse. This size distribution was expected to develop a char cake that would be less dense and less likely to sinter on the filter. It was also desirable to operate the process at steady state conditions with a narrow temperature range in the baghouse.

 Good process temperature control and steady state operation was achieved on all runs except the first. Figure 1 shows trends of key process temperatures for run M2-8, which was typical for the other runs as well. However, it was not possible to reach an equilibrium recovered pressure drop across the filter on any of these runs except for a portion of run M2-10; instead, this pressure drop continued to increase at a steady rate throughout the run as can be seen in figure 2 for run M2-8. The recovered pressure drop is defined as the pressure drop measured immediately after going through a backpulsing cycle to dislodge the accumulated filter cake. In typical baghouse filter operation, the recovered pressure drop initially rises rapidly and then asymptotically approaches a relatively constant value. In all of these runs the pressure drop eventually rose to a level that caused excessive pressure in the eductor area of the process which then disrupted the ability to feed smoothly. This increase in pressure drop across the filter is caused by the char that could not be removed from the filter by backpulsing. From a practical standpoint, the long term continuous operation of the process was limited by this pressure drop across the filter and occurred after processing 80 to 100 kg of feed per m^2 of filter surface. During these runs, we looked at changing baghouse temperatures, backpulse pressure and duration to more effectively remove the filter cake. However, as can be seen from figure 3, which shows the recovered pressure drop as a function of

the cumulative feed processed, these variables appeared to have no influence on the ability to remove the adhered char from the filters. The rate of pressure drop increase appears to be similar for all the runs regardless of the operating temperature or backpulse pressure and duration used.

Following the runs a dense permanent cake of char approximately 1-2 cm thick covered the entire surface area. On some runs, char bridged between the filter elements. The char could be scraped off in chunks or small sheets that easily crushed to a fine powder.

Fig. 1. Example of reactor exit and baghouse temperature profile for run M2-8

Fig. 2. Example of baghouse pressure drop profile for run M2-8

   Once this cake was established, filters had to be removed from the baghouse and vacuum cleaned _ a very time consuming process. The possibility of using controlled oxidation as a means of regenerating the baghouse was explored before runs M2-7, M2-8, and M2-9. New filter bags were installed prior to run M2-10 instead of oxidatively regenerating after run M2-9. The NEXTEL™ filter bag temperature could not exceed 760` C in the presence of alkali metal oxides, because at these temperatures the metal oxides melt and fuse the fibers of the NEXTEL™ cloth together, making it brittle [8]. The baghouse was configured with thermocouples located 1 cm from the bags to monitor the gas temperature during the oxidation. Since it was not possible to measure the actual bag temperature, we carried out the regeneration while maintaining a 600` C temperature at the nearest thermocouple. The temperature was easily controlled by introducing measured air flows into the nitrogen carrier gas stream while the baghouse was at temperature. During the oxidation process the baghouse was periodically backpulsed to speed up the char removal rate. Although this procedure permitted complete recovery of the baghouse initial pressure drop, it took between 6-9 hours to complete the regeneration. Initially

this appeared to be a viable method of regenerating the filters in the baghouse, however, further investigation indicated that this procedure may in fact lead to a faster rate of filter blinding (see discussion section).

Fig. 3. Baghouse Recovered Pressure Drop vs. Cumulative Feed Processed. The recovered pressure drop is measured immediately after the filters have gone through a back pulse cycle.

5 Oil Properties and Yields

Ultimate analyses of the oils from each run are shown in Table 1. Elemental compositions of the oils are very similar except for a slightly lower oxygen content in oils from runs M2-7 and M2-9. Yields are presented in Table 2 and show slightly higher water yields from these two runs. Heating values for these runs are also slightly higher, which would be expected with less oxygen.

   Trace element concentration was determined by instrumental neutron activation analysis and values are given in table 3. Alkali metal content of oils from runs M2-6, M2-7, M2-8, and M2-9 are very consistent but it is almost an order of magnitude lower in oil from run M2-10. M2-10 oil is the cleanest oil we have produced to date; the alkali metal levels almost achieving the 1 ppm maximum specified for a fossil-fuel derived turbine fuel. This low sulfur oil could probably be used in a turbine

without harm to the blades. The ash levels in the ultimate analysis appear to correlate well with the alkali metal concentration as determined by instrumental neutron activation analysis.

   The yields are not as high as those obtained on the original process operated at NREL [5,5a]. The coarser coalescing filters, which are not designed to recover all of the aerosols from the process stream, contribute to the yield losses but are necessary to minimize the overall system pressure drop. The higher relative carrier gas throughputs used in this process will also strip away more of the volatile compounds, in addition to some of the water, and send them to the process flare. However, these same gas throughputs have reduced the residence time in the baghouse by 41% (6 seconds to 3.5 seconds). Combined with the vortex reactor (0.3 sec) and transfer line (0.3 sec), the total gas/vapor residence time in the hot zone is about 4.1 seconds. At this lower residence time, losses due to cracking of the vapors should be reduced. The char yields appear to be linked to the biomass feed rates. On run M2-9 the actual feed rates were approximately 17 kg/hr whereas in the other runs the actual feed rate was closer to 24 kg/hr. At the higher feed rates, incomplete pyrolysis of the char was observed, which contributed to higher
char yields.

Table 1. Ultimate Analysis of Biocrude Oil Made From Hybrid Poplar

Component wt%	Poplar Feedstock	M2-6	M2-7
Moisture		18.9	19.6
Carbon	49.0	45.8	47.4
Hydrogen	6.0	5.3	5.3
Oxygen	44.1	28.9	27.5
Nitrogen	0.1	0.25	0.13
Sulfur	0.03	0.03	0.02
Ash	0.98	0.016	0.016
HHV MJ/kg	19.5	18.9	19.2
LHV MJ/kg	18.2	17.3	17.5
Viscosity @40°C cSt		46.5	50.4

Table 1. Ultimate Analysis of Biocrude Oil Made From Hybrid Poplar (Continued)

Component wt%	M2-8	M2-9	M2-10
Moisture	20.0	19.6	16.8
Carbon	45.6	47.0	48.1
Hydrogen	5.4	5.1	5.3
Oxygen	29.0	28.1	29.6
Nitrogen	0.05	0.09	0.14
Sulfur	0.02	0.04	0.04
Ash	0.018	0.018	0.007
HHV MJ/kg	18.5	19.1	18.8
LHV MJ/kg	16.6	17.5	17.3
Viscosity @40°C cSt	27.3	34.0	42.7

Table 2. Pyrolysis Product Yields From Hybrid Poplar

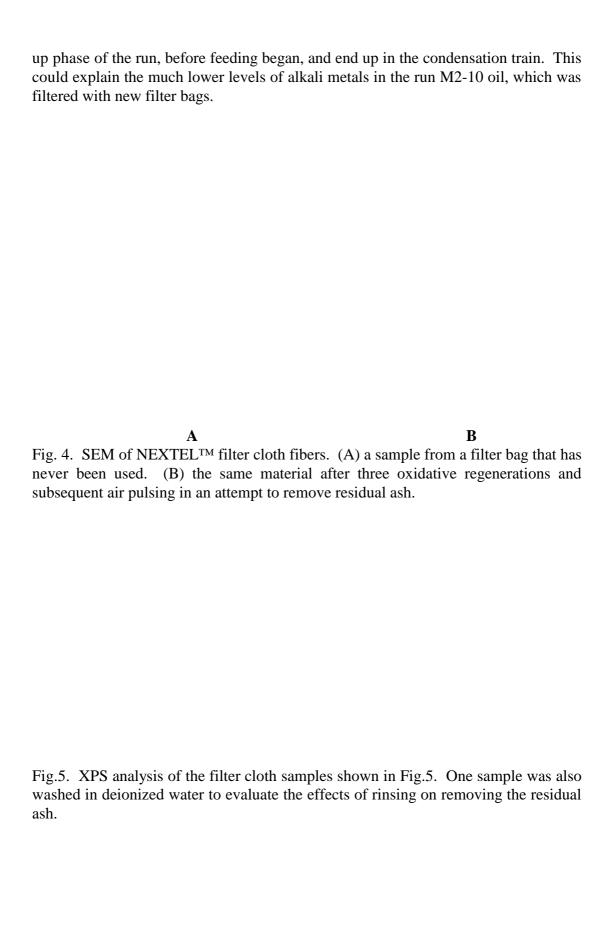| Yields wt% of feed (moisture free)	M2-6	M2-7	M2-8	M2-9	M2-10
Organic Liq.	39.0	41.8	36.8	44.1	46.2
Water	9.1	10.2	9.2	10.7	9.3
Char	23.3	24.1	27.6	14.7	19.9
Gas	N/A	13.1	15.8	N/A	14.1
Volatiles, H_2O (by difference)	N/A	10.8	10.6	N/A	10.5

Table 3. Trace Element Analysis of Biocrude Oil Made From Hybrid Poplar Feedstock

Element, ppm	M2-6	M2-7	M2-8	M2-9	M2-10
Calcium	6	4	3	4	1
Potassium	5	4	4	4	1
Sodium	4	2	2	1	0.9
Magnesium	<3	3	1	4	0.7
Chlorine	8	3	3	3	11
Aluminum	2	1	1	1	0.3
Titanium	<.2	0.7	0.2	0.2	0.2
Vanadium	0.01	0.01	0.01	0.01	<0.01
Manganese	0.2	0.2	0.1	0.06	0.04

6 Discussion

The rate at which the filters blinded progressively worsened after each oxidative regeneration of the baghouse. The final baghouse pressure drop, measured after a full cycle of backpulses (4), was plotted against the net cumulative feed. It can be seen from these data, in figure 3, that the initial rate of increase is much steeper for the three runs that were preceded by an oxidative regeneration of the baghouse. To investigate the possibility that the temperature of the filter bag fibers exceeded 760` C we removed a small test sample from one of the filter bags after run 9. This sample was then oxidized under controlled conditions to simulate regeneration in the baghouse, and then cut in half. One piece was subjected to air pulses through the fabric to remove residual ash fines (as would be done in the baghouse); the other piece was thoroughly washed in deionized water to remove any residual ash. The samples were then examined by SEM and XPS microprobe techniques to evaluate their surface characteristics. The SEM micrographs in Figure 4 clearly show very small particles on the surface of the air-pulsed sample and none on the new bag sample. Results from the XPS analysis are shown in Figure 5 and indicate that both the air pulse and washed samples have more potassium and calcium on the surface relative to a new, never-used bag. The XPS results suggest that the particles are ash remaining from the char oxidation. Ash present during biomass pyrolysis has been reported to polymerize pyrolysis intermediates to produce more char [10]. A similar effect has also been reported for the char itself [11,12] when biomass pyrolysis vapors are passed over it. Thus, pyrolysis vapors may be catalytically reacting with the ash present on the surface of the filter and also with the char in the filter cake. These reactions may contribute to physical changes in the char cake that cause it to become more difficult to remove as the run progresses. The initial high rate of pressure drop increase may be due primarily to the ash on the fibers catalyzing char (coke) formation reactions that plug the interstices of the filter cloth. A similar phenomenon may also occur in the char cake, but at a slower rate because the alkali in the char is only partially exposed at the surface [12]. The relatively low rate of recovered pressure drop increase seen for run 10, particularly in the early part of the run, is thought to be due to the use of virgin filter bags. However, even at the later stages of this run the recovered pressure drop is beginning to climb. The humps seen in the curves followed periods of multiple backpulse cycles. During these cycles, small sheets of char could have been dislodged from the filters to give greater pressure drop recoveries but would more quickly reload with char because the gas/vapor stream would preferentially pass through this area of lower resistance. Once reloaded, the recovered pressure drop should follow its previous path. This explanation is consistent with the data shown in Figure 3. The recovered pressure drop also begins to rise more steeply at the end of runs 6,7,8,and 9 as would be expected when the reactive char cake thickness grows and cannot be removed from the filter.

  The ash remaining on the filter cloth fibers may also be contributing to the differences in ash, and consequently alkali levels, in the oils produced from this series of experimental runs. Some of this ash could have passed through the bags during the heat-

up phase of the run, before feeding began, and end up in the condensation train. This could explain the much lower levels of alkali metals in the run M2-10 oil, which was filtered with new filter bags.

A   **B**

Fig. 4. SEM of NEXTEL™ filter cloth fibers. (A) a sample from a filter bag that has never been used. (B) the same material after three oxidative regenerations and subsequent air pulsing in an attempt to remove residual ash.

Fig.5. XPS analysis of the filter cloth samples shown in Fig.5. One sample was also washed in deionized water to evaluate the effects of rinsing on removing the residual ash.

7 Conclusions

Biomass pyrolysis oils having alkali metal concentrations below 10 ppm can be reproducibly made when employing hot gas filtration. However, it becomes progressively more difficult to dislodge the accumulated permanent char cake on the filter as more feed is processed. Standard baghouse filter operating techniques have proved ineffective in removing this char, especially when the cake thickness becomes greater than 1 cm.

   Although it is possible to oxidatively regenerate the baghouse filter to recover the initial pressure drop, this technique also leaves residual ash on the surface of the filter cloth fibers that appears to exacerbate the rate of filter blinding. Given these observations and the known reactivity of biomass ash, oxidatively removing char from any type of hot gas filter is not recommended. The char cake itself also appears to promote a progressively higher pressure drop across the hot gas filter, although at a lesser rate than ash.

   A more fundamental understanding of events within the char cake as biomass pyrolysis vapors pass through will be important in developing methods for long-term operation of hot gas filters.

8 Acknowledgments

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